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Entrained flow gasification of biocoal from hydrothermal carbonization

Alexander Tremel [a,*], Jan Stemann [b], Michael Herrmann [a], Berit Erlach [b], Hartmut Spliethoff [a]

[a] *Institute for Energy Systems, Technische Universität München, Boltzmannstraße 15, 85748 Garching, Germany*
[b] *Institute for Energy Engineering, Technische Universität Berlin, Marchstraße 18, 10587 Berlin, Germany*

HIGHLIGHTS

- ▶ Biocoal was produced by a mild hydrothermal carbonization of beech wood.
- ▶ Biocoal pulverization was found to be much less energy intensive compared to wood.
- ▶ In entrained flow gasification of biocoal a high level of conversion was achieved.
- ▶ Gasification of lignite indicates that biocoal can be used as a renewable substitute.

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ABSTRACT

Hydrothermal carbonization (HTC) converts biomass into a coal-like substance, here referred to as biocoal. Beech wood chips are treated hydrothermally at 210 °C for 3 h in a 250 L pilot scale reactor. The carbon content (daf) thereby increases from 48 wt.% to 57 wt.% and the volatile matter (wf) decreases from 79 wt.% to 69 wt.%. The carbon and energy yields are both 80% on a mass and HHV basis, respectively, with the major loss being solubilized substances. Pulverization of biocoal is found to be much less energy intensive compared to wood. Moreover, pulverized particles show a spherical shape which may facilitate fluidization.

Gasification experiments are carried out at temperatures of 1000 °C, 1200 °C and 1400 °C at atmospheric pressure in a laboratory scale entrained flow reactor. The standard particle diameter used in the experiments is 80–160 μm. During each experiment char samples are collected and the synthesis gas concentration is measured. Carbon conversion at a residence time of 1.0 s is 84%, at both 1000 °C and 1200 °C. A significant increase in carbon conversion to 88% at 1400 °C is observed. Comparable gasification experiments are carried out with lignite as the fuel. Rhenish lignite is gasified using the same stoichiometry and particle size. The conversion of lignite is slightly lower indicating the high reactivity of biocoal.

An increase of particle size would be beneficial due to the lower power consumption for pulverization. In experiments with biocoal at a particle size of 160–250 μm, a slightly lower conversion is measured due to internal and external mass transfer limitations at the particles. The high conversion at short reaction times indicates a high reactivity of biocoal under entrained flow gasification conditions.

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1. Introduction

The utilization of biomass in industrial and energy applications offers a wide range of potentials. Deploying biomass as a fuel for heat and power production enables the reduction of CO_2 emissions compared to fossil resources. Biomass energy with carbon capture (BECCS) is increasingly discussed as an important contributor to low GHG stabilization targets [1], since it can produce negative net CO_2 emissions. Contrary to solar and wind power biomass is easily storable and can produce electricity on demand. Furthermore, biomass can be used as a feedstock for industrial products (e.g. plastics and polymers) and transport fuels, thereby displacing fossil oil and gas.

1.1. Entrained flow gasification

For the energy and industrial applications, thermal gasification is a promising technology. Solid feedstock is converted to a synthesis gas that can be used as the feed material for both chemical synthesis and power production. Entrained flow gasification is arguably the most suitable of the gasification technologies, since its low residence time allows compact gasifiers and the high operating temperature provides a high quality, tar-free syngas.

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* Corresponding author. Tel.: +49 (0)89 289 16268; fax: +49 (0)89 289 16271.
E-mail address: tremel@tum.de (A. Tremel).

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Entrained flow gasification of coal is an industrial technology, with several large scale units of several hundreds MW_{th} in operation. The US Department of Energy has databased all existing and projected larger scale gasification facilities [2]. From 2005 until today, 94% of all registered gasifiers worldwide, in operation or planned, are based on entrained flow gasification. However, almost all gasifiers are designed for coal or pet coke as a feedstock. Despite its high development stage, ash and conversion related problems in entrained flow gasifiers still exist and are being investigated [3].

The application of entrained flow gasification for biomass creates two major challenges: ash handling and fuel preparation of biomass. Entrained flow gasifiers are typically operated above the ash melting temperature. Liquid slag is formed that protects the gasifier wall from corrosion and enables a stable and steady drain of ash. It is not clear, whether a stable slag layer forms with woody biomass that has a low ash content and a high ash melting temperature [4]. Despite of the presence of low-melting alkali compounds, an ash with a high melting temperature is formed due to the volatilization of these compounds into the gas phase [5]. In coal gasification, flux materials (minerals) are used to enhance the rheological properties of slag. The addition and possibly recycling of flux material or the co-gasification with coal may be a viable option for the entrained flow gasification of biomass or biocoal. Alternatively, a non-slagging reactor operates below the ash melting temperature. But even at a lower temperature of 1200 °C, partial melting of the biomass ash components cannot be avoided leading to stickiness and the blockage of the gasifier [6]. The expected high reactivity of biocoal may allow a decrease of operation temperature below the melting temperature. The temperature is decreased by feeding less oxygen to the gasifier wich would improve the efficieny of the process. First, the energy demand for oxygen production is lowered and secondly the heating value of the product gas is increased as less fuel has to be burned in the autothermal process to provide thermal energy for gas heat-up. However, for the evaluation of the best operation mode (slagging or non-slagging), reactivity data for biocoal at high temperature are required, but so far not available.

The second major challenge for the entrained flow gasification of biomass is fuel pulverization. The particle size requirements are dependent on the fuel reactivity and fluidization behavior. For entrained flow gasifiers with a dry feeding system, the fuel (coal) particles are fed to a fluidized bed and then transported pneumatically to the burner. Fluidization of the coal particles is required to achieve a steady mass flow rate of the gasifier feed [6]. The fluidization behavior is dependent on the particle size and shape and typically improves with smaller particle size. However, the fibrous structure of milled wood leads to bridging of particles, which impedes smooth pneumatic transport [7,8]. Indeed, tests with a lab-scale pneumatic feeding system indicated that wood powder is not suited for pneumatic feeding [6]. Since fluidization behaviour is crucial for entrained flow gasification, torrefaction has been suggested as a pretreatment for biomass to improve its fluidization properties. Bergman et al. [9] tested fluidization properties of willow wood after a mild torrefaction at 270 °C and proved that particles with a diameter of approximately 30–400 μm can be fluidized smoothly. This is mainly caused by a change in particle structure, because torrefied and pulverized wood fibers are shortened and particles become more spherical. Consequently, the fluidization behavior is improved by a mild thermal pretreatment process.

The residence time of coal particles in an entrained flow gasifier is low, typically lower than 10 s. In order to achieve a high conversion within this short time, coal particles are pulverized to some hundred microns [10]. Knowledge about the particle size requirements for complete conversion is limited since only a few studies have analyzed the reactivity of biomass under entrained flow gasification conditions (e.g. [6,11–14]). van der Drift et al. [6] concluded that a biomass particle size <1 mm should be suitable for entrained flow gasification. However, Hernández et al. [13] report that a significant increase of conversion in an atmospheric entrained flow gasifier was observed when decreasing the particle size from 1 mm to <500 μm. Beech wood particles in the size fraction 80–200 μm were found to achieve complete conversion in a steam atmosphere at 1400 °C after 2 s [14].

For comparison, the particle size requirements in an industrial scale gasifier for soft brown coal are 55% <100 μm and 99% <500 μm [10]. Due to the high reactivity, the required particle size for biomass gasification is likely to be in the range of brown coal or even above. The power demand for biomass pulverization can be high. Milling wood to 100 μm was found to consume five times more electricity per MJ of feedstock than coal [8]. A thermal pretreatment process, such as torrefaction or HTC, is expected to substantially reduce the power consumption due to a breakdown of the fibrous structure.

1.2. Hydrothermal carbonization

In summary, biomass pretreatment processes have the potential to improve fluidization behaviour, reduce the energy demand for pulverization and increase the energy density and homogeneity of the feedstock. This paper investigates HTC, one such upgrading process which is currently in the research and development stage. The HTC reaction takes place in pressurized water at 200–250 °C at or above saturation pressure and is slightly exothermic. Because the process takes place in water, HTC is well suited for wet biomass. Laboratory scale experiments have been conducted with a wide range of feedstock, including wood, straw, grass, municipal waste, digestate from anaerobic fermentation and bark mulch [15,16].

During HTC, oxygen is removed from the feedstock by decarboxylation and dehydratisation reactions, thus increasing the C/O ratio. The degree of carbonization increases with temperature and residence time. The higher the degree of cabonizazion, the higher the calorific value of the biocoal, but the lower the mass and energy yield, since more of the feedstock energy is converted into heat of reaction. Higher heating values (HHV) of 25 MJ/kg (dry basis) were reached within 4 h at an operating temperature of 220 °C in laboratory experiments with poplar wood [17].

Treating biomass with HTC facilitates mechanical dewatering, which is much less energy intensive than thermal drying. In lab-scale experiments with a laboratory piston press, dry matter contents of 60–70% were achieved [17]. Simulation studies for a continuous HTC process design including preheating and pressurizing of the biomass slurry, biocoal depressurizing and cooling, mechanical dewatering and drying of the biocoal to a final water content of 10% suggest an overall energetic efficiency of 75–85% on an HHV basis [18–20]. Based on the LHV, even higher efficiency is feasible for biomass with a high moisture content.

Bergman et al. [9] propose that during torrefaction a destabilization of fibres is induced by a shortening of individual cellulose chains and that this is due to the depolymerization rather than the decomposition of cellulose. The temperatures for degradation of biomass is considerably lower for HTC than for torrefaction [21] which can be explained by the hydrolysis of plant constituents during HTC. The main mechanism appears to be the cleavage of ester and ether bonds between monomeric sugars by the addition of one molecule of water [22]. Similar to the torrefaction, depolymerization of cellulose during HTC begins at lower temperatures than degradation. Therefore, good grindability and more spherical particles can be expected for HTC derived biocoal, but at lower process temperatures than for torrefaction.

Improved grindability, a less fibrous structure and increased calorific value and energy density make HTC look promising as a pretreatment process for the entrained flow gasification of biomass. However, there is no experimental study known to the authors that analyses the reactivity of HTC derived biocoal in a high temperature entrained flow reactor. The objective of this work is to investigate the conversion behavior of HTC derived biocoal under such conditions.

2. Hydrothermal carbonization

2.1. Experimental setup and procedure for HTC

Beech (*Fagus*) wood chips with a particle size of 2.5–3.5 mm are hydrothermally carbonized in a pilot batch reactor at 210 °C. The HTC reactor has a volume of 250 L and is made of P 250 GH carbon steel. The experimental set-up is depicted in Fig. 1. 14.7 kg of wood chips (dry mass) are filled into the reactor and 16.5 kg of water are added. The reactor is heated by direct injection of saturated steam at 250 °C and hence the water to biomass mass ratio steadily increases to 7 at the end of the process. The reactor reaches 210 °C after 1 h and the temperature is maintained for 3 h at 210 ± 3 °C, controlled by a PID controller and a control valve for the steam flow. The reactor is subsequently emptied semi-continuously via a water cooled lock hopper in which the biocoal slurry is cooled to 40 °C. The slurry is dewatered in a filter press with a pore diameter of 300 μm to 80% water content. Emptying takes 2 h during which the reactor cools to 180 °C. Afterwards the reactor is flushed with press water and is emptied again. The entire procedure is repeated five times and a mixed sample is used for subsequent gasification. Mass and energy balances of the HTC process are shown in Table 1.

2.2. Characterization of HTC derived biocoal

Compositions of parent wood, biocoal and the Rhenish lignite used in the entrained flow experiments are presented in Table 2.

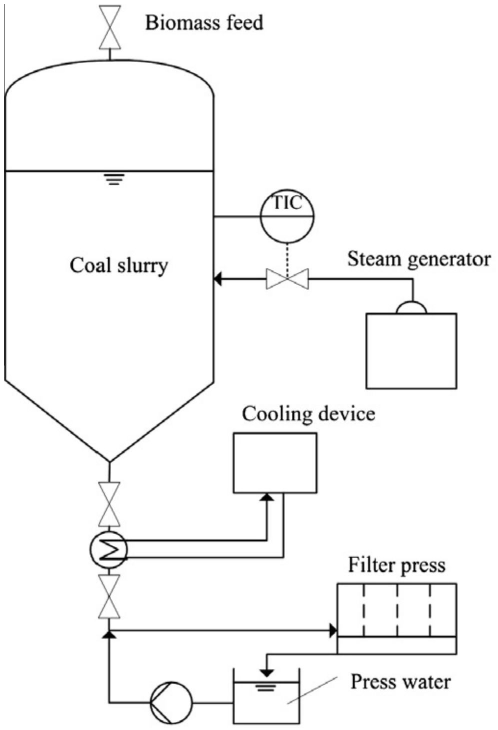

Fig. 1. Experimental setup for hydrothermal carbonization.

Table 1
Mass and energy balances of carbonization experiments (mean values with the standard deviation shown in parenthesis).

Wood (dry) (mass(g))	Water (mass(g))	Biocoal (dry) (mass(g))	Liquid phase		Solid yield (–)	Energetic yield (HHV) (–)
			Mass (g)	TOC (mg/L)		
14,700 (120)	n.a.	9980 (860)	104,500 (12,200)	9620 (360)	0.68 (0.06)	0.81 (0.08)

Under the experimental method just presented, the biocoal composition can be well reproduced whereas the solid yield fluctuates by 10%. This is probably because some of the biocoal remained at the walls of the reactor although it was flushed with water after emptying. Laboratory experiments under the same reaction conditions result in a solid yield of 0.666 ± 0.009 on a mass basis and a slightly higher carbon concentration. Approximately 80% of the carbon in the biomass is recovered in the biocoal and 15% remains solubilized in the liquid phase. By decreasing the water to biomass ratio and by recycling of process water the carbon and energetic yield can be increased [17]. In our experiments a rather low temperature of 210 °C for 3 h is applied. An increase of the HTC reaction temperature would result in a significant increase of the carbon content and calorific value, but on the other hand would lead to a decrease in the energetic yield.

During the HTC process parts of the ash forming minerals are dissolved in water. The ash composition of the biocoal, however, depends on the biomass, mechanical dewatering, process water recirculation and pH. In experiments with poplar leaves, potassium was dissolved to a large extent whereas calcium remained in the biocoal [17] or was dissolved to a lesser extent [23]. The HTC process could change the ash fusion temperature that is a critical design parameter in entrained flow gasification. It determines roughly the minimum temperature required to operate the gasifier in slagging mode. Ash fusion characterization comprises the following characteristic temperatures:

- Shrinkage starting temperature (SST).
- Deformation temperature (DT).
- Spheric temperature (ST).
- Hemisphere temperature (HT).
- Flow temperature (FT).

We performed the ash fusion characterization according to two slightly different standards: one for coal [DIN 51730] and one for biogeneous fuels [DIN CEN/TS 15730-1]. The definition of FT differs between the two standards. The characteristic temperatures for the ash melting behavior of biocoal are shown in Fig. 2. Shrinkage starting (SST) is detected at 786 °C. Deformation begins at 1175 °C

Table 2
Proximate and ultimate analysis of biomass, biocoal and lignite.

	Wood	Biocoal	Lignite
Proximate analysis			
Moisture (wt.%)	7	4	10
Ash (dry) (wt.%)	1	1	6
Volatile matter (dry) (wt.%)	79	69	51
Ultimate analysis			
C (wt.% (daf))	48.1	56.9	67.8
H (wt.% (daf))	6.5	5.7	5.2
N (wt.% (daf))	0.1	0.3	0.8
S (wt.% (daf))	0.1	0.2	0.8
HHV (MJ/kg)	19.2	22.9	27.7

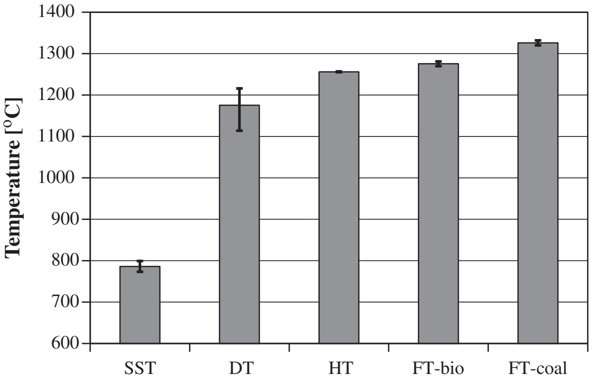

Fig. 2. Characteristic ash fusion temperatures for biocoal according to different standards. The error bars denote minimum and maximum values from repeated measurements.

and a complete melting of the ash sample is observed at 1276 °C (biomass standard) and 1326 °C (coal standard), respectively. As the ash melting temperature aligns well with published data for beech wood [4], a significant influence of the HTC process on the ash fusion temperature is not observed. Slagging mode operation of the gasifier is expected to be feasible at approximately >1300/1400 °C. For non-slagging mode, the gasifier has to be operated at a sufficiently low temperature in order to prevent any ash agglomeration due to stickiness. This could require temperatures below the ash deformation temperature (DT) of 1175 °C. Shrinkage of the ash sample at 786 °C indicates that ash reactions occur at an even lower temperature. At this temperature, the shrinkage is expected to be caused by the partial or full evaporation of alkali compounds. This will also occur at higher temperature in an entrained flow process. The evaporation of alkali compounds increases the ash melting temperature of the remaining mineral matter. Therefore, the deformation temperature (DT) 1175 °C rather than the shrinkage starting temperature (SST) is an upper limit for the operation temperature of a non-slagging gasifier. The fact, that ash melting for woody biomass does not occur in the range of the SST, is also proven by fluidized bed gasifiers. These are operated in the range 800–900 °C and ash melting would prevent stable fluidization due to bed agglomeration. The stable non-slagging operation of an entrained flow biocoal gasifier is assumed to be possible at a temperature below or around the ash deformation temperature of 1175 °C.

2.3. Biocoal pulverization

2.3.1. Energy demand

The energy demand for coal pulverization is strongly dependent on coal quality. According to supplier information, the electricity consumption for large scale coal mills is 36–54 kJ/kg [Information by LOESCHE GmbH, Germany]. This is in agreement with data from literature (25–130 kJ/kg) for a wide range of coals [24].

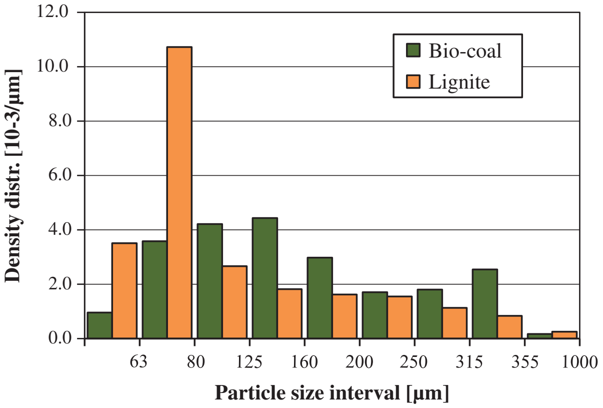

Fig. 4. Particle size density distribution of biocoal and Rhenish lignite after pulverization in a cross hammer mill.

Pulverization experiments of biocoal in a larger scale were carried out using a pin mill (Nara Jiyu Mill M-3). Poplar wood was carbonized at the same reaction conditions as described above and 5–20 mm sized biocoal particles were dried to 5% water content before milling. A mass fraction of 97.3% could be pulverized to particles <280 µm at a feed rate of 1.65 kg/min and at a power consumption of 3.7 kW. This results in a throughput of 100 kg/h and a specific energy consumption of 135 kJ/kg. This is comparable to torrefied wood, where the specific energy consumption for milling to a comparable particle size is 140 kJ/kg and much less than for willow at 700 kJ/kg [25].

2.3.2. Particle shape

To analyze the particle shape after milling, raw biocoal and its parent wood are pulverized in a planetary mill (Retsch PM100) and sieved (mesh width 240 µm). Fig. 3 shows the characteristic fibrous and elongate structure of milled wood whereas the biocoal particles demonstrate a rather spherical shape. This indicates that biocoal particles presumably break in multiple directions during pulverization and not preferably along the orientation of the macrofibrils. The particle shape after HTC suggests an improvement of fluidization behavior.

2.3.3. Particle size distribution

Raw biocoal with a water content of 10% and a particle size <4 mm is pulverized in a cross hammer mill with a 1 mm sieve insert. For comparison, Rhenish lignite is ground using the same procedure and moisture content. The particle size density distribution of biocoal and lignite after milling is shown in Fig. 4. Pulverized coal is classified using a sieve tower and the particle size denotes the mesh width for the sieve plates used. For both fuels, the particle size distribution is similar but biocoal seems to be slightly

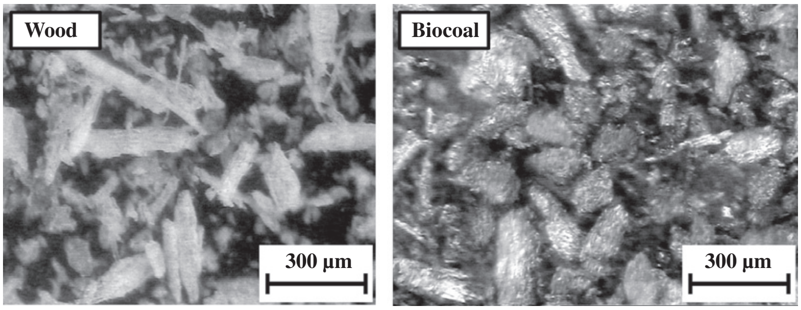

Fig. 3. Microscope image of pulverized wood (left) and biocoal particles (right) after pulverization in a planetary mill.

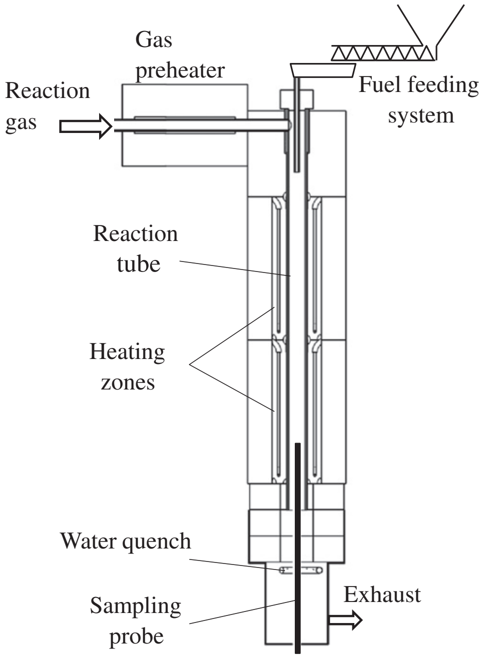

Fig. 5. Sketch of the Baby High Temperature Entrained Flow Reactor (BabiTER).

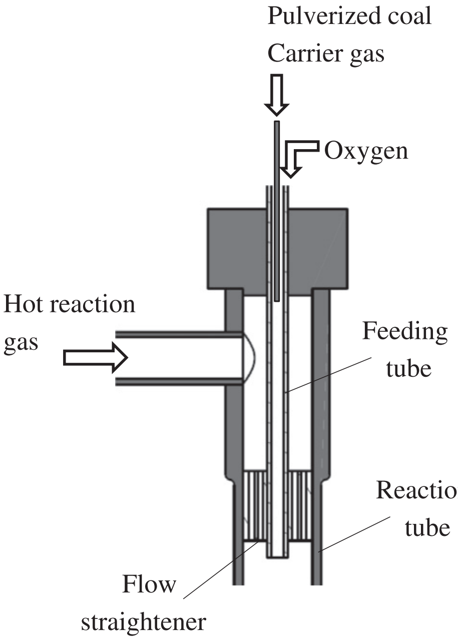

Fig. 6. Particle and gas injection system of the BabiTER.

shifted toward larger particle sizes. Notwithstanding, 80 wt.% of lignite and 79 wt.% of biocoal, respectively, is milled to a particle size of 250 μm or less. As a cross hammer mill is not suitable for the pulverization of wood or other lignocellulosic biomass, these milling results indicate the advantage of hydrothermal carbonization on pulverization properties.

3. Gasification experiments

3.1. Experimental setup – entrained flow reactor

The experimental facility used in this work is the Baby High Temperature Entrained Flow Reactor (BabiTER). The facility is designed to study gasification reactions at conditions relevant to high temperature entrained flow gasifiers. Fig. 5 shows a schematic of the facility.

Different gases can be premixed and fed to the gas preheating unit. The gas flow rate of each gas is controlled by dedicated mass flow controllers (MFCs). The gas preheater consists of a horizontal ceramic tube surrounded by heating elements. The gas mixture can be heated to a maximum temperature of 1300 °C and then directly enters the reaction tube. Pulverized fuel is fed to the reaction tube from a dosing system at the top of the reactor. A constant fuel mass flow is achieved by a combination of screw feeder and vibrational chute and is controllable in the range 50–500 g/h. The dosing system is situated on a balance allowing an online monitoring of the fuel feed rate. To prevent air from entering the reactor through the feed line, the feeding system is enclosed in a container. Inert gas fed to the container is used as a carrier gas for the fuel particles. The gas and fuel mixing unit within the hot zone is shown in Fig. 6. Particles enter an inner tube (inner diameter 4 mm) with nitrogen as the carrier gas. Due to the small diameter a high gas velocity is achieved even for low gas flow rates. Pure oxygen is fed to the outer tube. The inner tube terminates within the transition to the hot zone and fuel particles are mixed with oxygen when entering the hot zone. The feeding tube within the reactor is heated by the hot reaction gas that enters the reactor from the side. The configuration is designed to simulate the conditions at the burner inlet of an industrial scale entrained flow reactor. Thus, very high heating rates comparable to industrial scale systems are achieved.

The main gas enters the reaction tube from the side and a laminar flow is achieved by a flow straightener. Shortly after the flow straightener, fuel particles enter the reaction tube. Due to the small diameter of the feeding tube the gas flow rate of the carrier gas is only 5–20% of the total gas flow depending on reaction conditions. The residence time of the particles in the hot section of the feeding tube is 30–60 ms resulting in partial pyrolysis of the particles before entering the reaction tube. Then, pyrolysis is completed and char-gas-reactions occur within the main reaction zone. The reaction tube has an inner diameter of 40 mm and a length of 1000 mm. By adjusting the gas flow rate, a defined residence time of the gas-particle-mixture within the hot zone is achieved.

After leaving the reaction tube, the hot gas and particle mixture is directly cooled by spray water from a ring-shaped nozzle. Gas and quench water are constantly removed from the quench zone.

Char and gas samples are taken from the hot reaction tube through a water cooled probe. This probe is inserted at the bottom of the quench zone and can be moved upwards into the reaction tube. By adjusting the height of the sampling probe char and gas samples are taken at different stages of conversion. At a given set of operation conditions (temperature, gas flow rate) char and gas samples with different residence times are taken along the reaction tube. Char is separated from the reaction gas in a char filter. A continuous gas flow from the sampling probe is analyzed using an NDIR/heat conductivity analyzer, and concentrations of CO, H_2, CO_2 and CH_4 are recorded.

3.1.1. Calculation of conversion

Carbon and overall conversions for each char sample are calculated using an ash tracer method. It is assumed that the ash remains in the char particle during conversion. This is confirmed by measuring the ash content at different temperatures in a muffle oven. As the major ash components (Al_2O_3, SiO_2, CaO) are not volatile under reaction conditions the error in conversion calculation is relatively small. This is confirmed in several other studies concerning coal and biomass gasification (e.g. [26–28]). Carbon and ash content is measured in a CHNS analyzer. Using the measured data, the carbon conversion and overall conversion are calculated. Given no volatilization of ash components, the average measurement uncertainty of carbon conversion is ±3 wt.% and the average measurement uncertainty of overall conversion is ± 2 wt.%, both within a 95% confidence interval.

3.2. Results of the gasification experiments

3.2.1. Biocoal conversion at high temperature

Prior to gasification, biocoal is pulverized in a cross hammer mill and, for most of the experiments, a particle size interval 80–160 µm is chosen. This particle diameter is in the range of particle size requirements for entrained flow gasification of lignite. To evaluate the influence of particle size on conversion, some experiments employed a 160–250 µm particle size interval. Following pulverization and sieving, the biocoal is dried at 40 °C to a moisture content of 4 wt.%.

The gasification experiments are carried out at varying temperatures and residence times and at a constant stoichiometry. The oxygen molar flow rate in the feeding tube and main gas are adjusted to the molar flow rate of carbon from the fuel feeding system. For each atom of carbon entering the reactor, one atom of oxygen is provided in the reaction gas resulting in an O/C ratio of 1. A constant fuel feed rate of 135 g/h is used in all experiments with biocoal.

Carbon conversion increases with temperature as shown in Fig. 7. Residence time in all diagrams denotes the average gas residence time within the reaction tube. In all experiments the gas flow forms a laminar profile in the reaction tube. Particles are injected and char samples are collected in the center of the tube where the gas flow velocity is above the average gas velocity. Therefore, the residence time of char particles collected through the sampling probe is likely lower than the average gas residence time. Flow profile calculations result an average particle residence time that is 40% lower than the average gas residence time.

At a gas residence time of 1.0 s in Fig. 7 there is no difference in conversion from 1000 °C to 1200 °C. At 1400 °C, the carbon conversion is 88%. The influence of residence time is shown for 1200 °C and 1400 °C. At an elevated temperature of 1400 °C, the increase in carbon conversion from 0.65 s to 1.0 s is higher indicating the effect of temperature on reaction rate. Due to the devolatilization of hydrogen, oxygen and trace elements (N, S, etc.), the overall conversion is significantly higher than the carbon conversion.

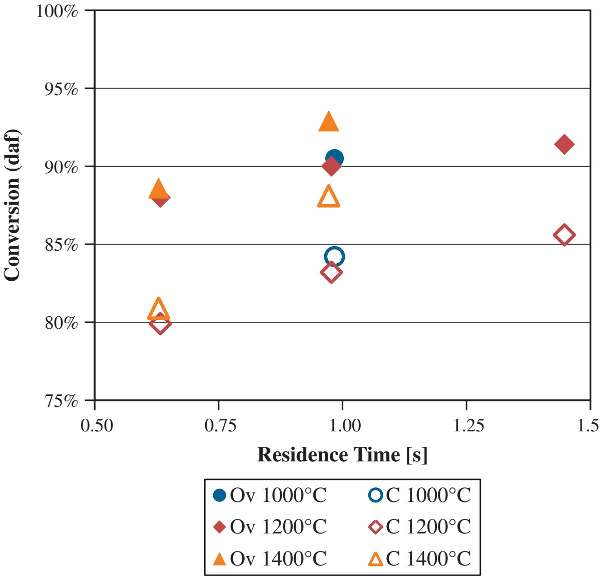

Fig. 7. Overall (Ov) and carbon (C) conversion for biocoal gasification at different temperatures and residence times (particle size 80–160 µm).

The experiments indicate a high reactivity of biocoal in entrained flow gasification conditions. Carbon conversion and overall conversion are high even at low residence time. Assuming a constant increase of conversion with residence time, complete conversion is likely to be achieved at a residence time <2 s at 1400 °C. This is in agreement with a recent study [14] that analyzed the gasification behavior of beech wood particles at 1400 °C with a comparable particle size fraction. At a temperature of 1200 °C, the time required for complete conversion is estimated to be less than 4s.

Pyrolysis is expected to take place within the feeding tube and in the beginning of the reaction tube. Due to the high concentration of volatile matter in biocoal (69 wt.% (daf) in the standard analysis), a high degree of carbon and overall conversion is achieved in the pyrolysis stage. The standard volatile matter content is measured at 900 °C. Certainly, volatile yield is dependent on pyrolysis temperature. Under entrained flow conditions, devolatilization in excess of the standard analyis was measured in several studies on coal and biomass pyrolysis (e.g. [26–28]). Therefore, volatile yield in the entrained flow experiments is expected to be higher than 70 wt.% (daf). However, pyrolysis reactions are fast and cannot be resolved within the reaction time range used here.

The concentrations of CO, CO_2 and H_2 are measured for each run. CO_2 and H_2O are the main products from volatiles combustion in the early stages of conversion. Then, during char conversion, solid carbon reacts with H_2O and CO_2 to form H_2 and CO. As H_2O could not be measured, the ratio of CO + H_2 to CO_2 can be used as an indicator for char conversion but also for gas quality. Gas quality is defined as

$$GQ = \frac{x_{CO} + x_{H_2}}{x_{CO_2}} \tag{1}$$

and is shown in Fig. 8. x_{CO,H_2,CO_2} denote the volumetric concentrations of the reaction gases. The concentration of CH_4 was also measured in each experimental run. As the concentration was always below the measurement uncertainty of the sensor (0.5 vol.%), the methane concentration is not considered in the gas quality calculation. The gasification of biocoal at high temperature results in a virtually methane free product gas.

The increase in gas quality with residence time is caused by proceeding char conversion and corresponds well with conversion shown in Fig. 7. But gas quality is also influenced by the homogeneous water gas shift reaction.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \Delta H < 0 \tag{2}$$

An increase in temperature shifts the chemical equilibrium to the left side. Therefore, the increase of gas quality from 1000 °C to 1400 °C is partly influenced by chemical equilibrium in the gas

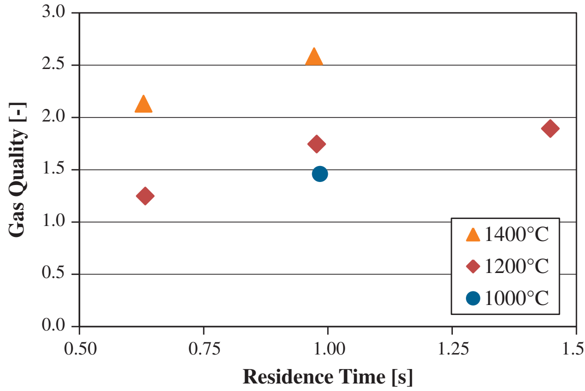

Fig. 8. Gas quality for biocoal gasification at different temperature and residence times.

Table 3
Difference between real gas quality and chemical equilibrium calculations.

Gasification temperature (°C)	Average deviation of gas quality from chemical equilibrium (%)
1000	29
1200	24
1400	7

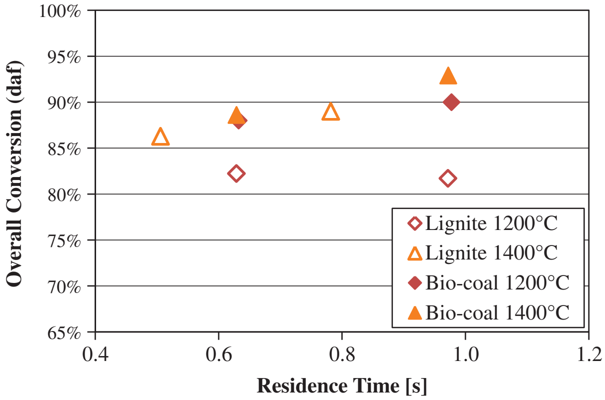

Fig. 9. Overall conversion for the gasification of lignite and biocoal (particle size 80–160 μm).

phase. However, the improvement of gas quality from 1000 °C to 1400 °C cannot be fully explained by equilibrium calculations. Gas quality is also influenced by char conversion and a high degree of char conversion is required for the production of a high grade synthesis gas.

Furthermore, theoretical gas quality is also estimated using chemical equilibrium calculations. The biocoal and gas flow rates and the char conversion data are used to calculate gas composition in chemical equilibrium at the gasification temperature of each run. The not converted carbon is subtracted from the biocoal flow rate before doing the equilibrium calculations. Therefore, only the elements that are converted to the gas phase are considered in the chemical equilibrium calculation.

The average deviation of the real gas quality from the theoretical gas quality is shown in Table 3. At low temperature there is a large deviation. The gas phase at a short residence time of 1.0 s and at at temperature of 1000 °C is not in equilibrium. At 1200 °C and a very short residence time (0.65 s) the deviation is 39%, but decreases to 16% at 1.45 s. The average value at 1200 °C is 24%. At 1400 °C gas data and equilibrium calculation are in agreement, the deviation both at 0.65 s and 1.0 s is 7%. The assumption of chemical equilibrium for the gas phase results in relatively high uncertainties at short residence times and low temperatures. At longer residence times, but especially at higher temperatures, the gas phase can be broadly predicted by chemical equilibrium.

3.2.2. Comparative experiments with lignite

Pulverized biocoal looks promising as a substitute for lignite in fuel conversion systems. Experiments with Rhenish lignite are therefore carried out at similar operation conditions. Fig. 9 shows the overall conversion of lignite gasification compared to biocoal. The coal feed rate of lignite is 200 g/h.

The overall conversion of lignite at 1200 °C is slightly lower than of biocoal. Volatile yields of lignite and biocoal are measured in a standard procedure at 900 °C and are 54 wt.% (daf) for lignite and 69 wt.% (daf) for biocoal. In a standard procedure volatile compounds remain in the vicinity of the char sample and therefore the recondensation of tar compounds is expected. Furthermore published experimental data for coal and biomass pyrolysis [26–28] show an increase of volatile yield with increasing temperature. Therefore, the overall conversion during pyrolysis in the entrained flow experiments at high temperature shown here is likely higher than in the standard procedure. As heterogeneous gasification reactions at 1200 °C are slow, overall conversion is mainly influenced by the release of volatiles and the slightly lower conversion for lignite can be explained by lower volatile yield during pyrolysis.

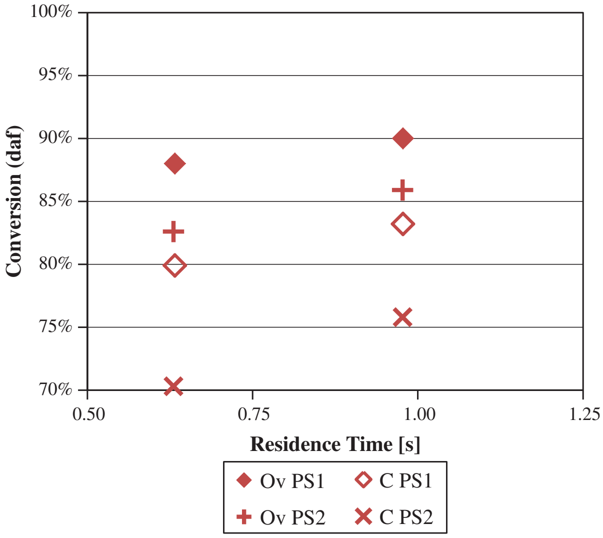

Fig. 10. Overall (Ov) and carbon (C) conversion for biocoal gasification at 1200 °C with different particle size (PS1: 80–160 μm; PS2: 160–250 μm).

At 1400 °C, overall conversion for lignite and biocoal are in good agreement. This may be caused by an increase in devolatilization of the lignite at higher temperature. The increase in conversion with residence time is a measure for the reaction rate of heterogeneous char reactions. Both fuels show a similar behavior indicating comparable reactivity at high temperature. Due to the similarity in reaction behavior, it is believed that biocoal can be used as a substitute in lignite gasification.

3.2.3. Influence of particle size

The power demand for fuel pulverization increases with decreasing particle size. The gasification experiments described thus far are carried out with a particle size of 80–160 μm. To evaluate the effect of particle size on conversion, larger particles (160–250 μm) are used. The overall and carbon conversion for the larger particle size (see Fig. 10) are significantly lower. Since particle size is not expected to significantly change the devolatilization of hydrogen and oxygen during pyrolysis, the effect of particle size on carbon conversion is higher than on overall conversion. At the high temperatures used in the experiments, the reaction rate is likely to be influenced by mass transfer limitations arising from boundary layer diffusion and pore diffusion. These diffusion limitations increase with particle diameter. However, the conversion of particles in the range 160–250 μm is still high. The overall conversion at 1200 °C and 1.0 s is 86%.

4. Conclusions

Hydrothermal carbonization is a mild thermal process used to improve the fuel properties of wet lignocellulosic biomass which does not require drying before treatment. The product biocoal is potentially a substitute for lignite and other coal types in large scale combustion and gasification processes. Entrained flow gasification, a particularly promising application for biocoal is explored in this paper.

4.1. Hydrothermal carbonization

To this end, beech wood chips are hydrothermally carbonized at 210 °C for 3 h. As a result, the carbon content (daf) increases from 48% to 57% and the volatile matter (wf) decreases from 79% to 69%. The carbon and energy yield is 80% with the major loss being solubilized substances. By recycling of the reaction water, higher biomass concentrations, or utilization of the solubilized substances, this loss can potentially be reduced in an industrial scale process.

4.1.1. Pulverization

Biocoal was pulverized using three different procedures (pin mill, planetary mill, and cross hammer mill) and all results indicate that biocoal is suitable for milling to a small particle size. For a direct comparison, raw biocoal and Rhenish lignite are pulverized in the same cross hammer mill. As the milling procedure for biocoal shows no additional complications compared to lignite a relative simple pulverization of biocoal in a larger scale can be expected.

4.1.2. Entrained flow gasification

At high temperatures, even short residence times produce high levels of conversion for particles in the range 80–160 μm. At a residence time of 1.0 s the overall conversion on a dry ash free basis is 90% (1000 °C/1200 °C) and increases to 93% at 1400 °C. Gas quality – defined as the ratio of $H_2 + CO$ to CO_2 concentrations – increases with residence time, but more strongly with temperature. Gas concentrations and gas quality at low temperature cannot be predicted by chemical equilibrium calculations but the deviation becomes marginal at 1400 °C.

Comparable entrained flow gasification experiments are carried out using lignite as a fuel. The experiments indicate a similar rate of the heterogeneous char reactions at high temperature for both fuels. It is expected that biocoal can be used as a substitute in entrained flow coal gasification facilities.

The ash fusion experiments of biocoal indicate that the operation in a non-slagging mode is feasible around or below the ash deformation temperature of 1175 °C. Due to the high reactivity, an entrained flow process below the ash melting temperature is a viable option.

The results of this work show the potential for the combination of hydrothermal carbonization and entrained flow gasification for biomass conversion. The pretreatment process improves biomass properties like energy density, grindability and particle shape and allows for the production of a standardized fuel. The high carbon and overall conversion of biocoal measured at low residence time and high temperature (1000–1400 °C) shows the potential of this new fuel for entrained flow gasification.

While in this work beech wood was used as a parent biomass for HTC, future gasification experiments should also be conducted with biocoal derived from different types of waste biomass, which are more likely to be an economically viable feedstock for HTC. Like entrained flow gasification of biomass or biomass derived fuels, the HTC process is still in an early state of development, and efficient industrial-scale operation still needs to be demonstrated.

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